

# van der Waals interaction of a molecule with a semiconductor surface not in equilibrium

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The characteristic features of the van der Waals interaction between a molecule and a nonequilibrium semiconductor has been studied. An approach to the calculation of the interaction energy, based on the “fluctuation-diffusion” relations, is proposed. It is shown that a nonequilibrium state of an adsorbent can change the character of the adsorption potential of a semiconductor surface. [S0163-1829(98)08939-5]

## I. INTRODUCTION

It is well known<sup>1-8</sup> that the state of a single adsorbed molecule on the surface of a solid is dependent on the nature of the adsorption bond. In the case of physisorption, this bond is maintained by polarization forces. For molecules with a weak static polarizability these are considered mostly as van der Waals (dispersion) forces. The adsorption potential is the important characteristic of adsorption which defines, in particular, the type of adsorption. It is usually assumed that the physisorption potential for nonpolar molecules is determined basically by van der Waals attractive forces and short-range repulsive forces.<sup>1,4,7</sup> Usually the adsorption potential  $U(l)$  is calculated only for a single molecule at the surface. In recent years, the interparticle interactions have been taken into account in the study of adsorption processes.<sup>9,10</sup> It should be pointed out that the interaction between a flat surface and a particle was not the only thing studied. For example, in Ref. 11 the van der Waals interaction between a molecule and a spherical cavity in a metal was discussed.

All the research known to the authors has been devoted to adsorption on the surface of a solid in the equilibrium state. But there is a possibility of adsorption of particles on a surface of a solid not in equilibrium. In particular, adsorption of molecules on the surface of a semiconductor not in the equilibrium state due to external optical pumping or through applying dc current may occur. It is clear that this problem is not only of theoretical interest but has practical application as well, since it opens an additional possibility to control adsorption properties of the surface. The van der Waals component of the adsorption potential for adsorption of a single molecule on the surface of a nonequilibrium semiconductor is calculated in this work. Characteristic properties of the formation of the van der Waals part of the adsorption potential are discussed.

In the case of adsorption of a particle on a surface in equilibrium, the calculation of the van der Waals component of the adsorption potential can be performed with the methods developed in Refs. 12 and 13, using the Callen-Welton theorem.<sup>14</sup> In the case of adsorption on the surface of a semiconductor which is not in the equilibrium state, the “fluctuation-dissipation” (Callen-Welton) theorem becomes

invalid for the calculation of the “field-field” type correlation functions. For this reason, we propose using the so-called “fluctuation-diffusion” relation,<sup>15-17</sup> which connects a correlator of the fluctuating values in the system with the diffusion processes. This effectively leads to smearing of the fluctuations. This approach is fruitful for the study of the formation of the van der Waals component of the adsorption potential by the Green’s-function method. We shall assume that long-range electrodynamic properties of the nonequilibrium semiconductor can be accounted for in terms of the dielectric formalism. This approximation allows us to introduce a dielectric function for the description of the adsorption properties on the surface of a nonequilibrium semiconductor.

There are situations when a nonequilibrium state in a semiconductor may be characterized by an effective electronic temperature  $T_e$ .<sup>18</sup> The electron distribution function in these cases has the same form as for the equilibrium (with  $T \rightarrow T_e$ ) state. One could assume that the Callen-Welton theorem should be adequate for such cases of nonequilibrium states. But, strictly speaking, due to the strong mutual interference between fluctuation currents and the energy of the electrons, the use of the Callen-Welton theorem is problematic. We propose other relations connecting the correlators of the “current-current” type to macroscopic characteristics of the system. For example, these could be the fluctuation-diffusion relations.

## II. CONNECTION BETWEEN THE ADSORPTION POTENTIAL AND CORRELATORS OF THE “CURRENT-CURRENT” AND “FIELD-FIELD” TYPES

A molecule situated at a distance  $l$  from the surface of a semiconductor will be considered. We suppose that the molecule is bound to the surface by physisorption. No chemical bonds are considered here. Consider the spontaneously fluctuating dipole moment  $p_i^{(sp)}$  of the molecule. This dipole moment induces a polarization in the adsorbent,  $p_i^{(ind)}$ . As a result of the polarization of a substrate, the self-acting field will occur at the molecule, given by

$$E_i^{(1)}(\mathbf{r}_a, l, t) = \delta \int dt' G_{ij}(0, l, l, t-t') p_j^{(sp)}(\mathbf{r}_a, t'), \quad (2.1)$$

with  $\mathbf{r}_a$  the position vector of the molecule in the  $XOY$  plane of a Cartesian system. We take the plane to coincide with the plane surface of the adsorbent, and take the  $OZ$  axis as directed out of the substrate. For simplicity, the position vector  $\mathbf{r}_a$  can be chosen to be equal to zero. In Eq. (2.1),  $G_{ij}(0, l, l, t-t')$  is the electrodynamical Green's function (photon propagator) of the system without a molecule.

In Eq. (2.1) the notation  $\delta$  means that the part which would appear when the molecule would be removed to infinity from the surface is neglected in the integrand. Since the interaction between the molecule and the surface occurs through the transverse part of the electrical field,<sup>19</sup> only the transverse part of the photon propagator in Eq. (2.1) is used. The Green's function of a system with an interface consists of two parts:<sup>20</sup> the first part,  $g_{ij}$ , provides the necessary singularity in the point of location of a source of the field; the second part,  $I_{ij}$ , serves to satisfy the boundary conditions at the interface. In other words,  $g_{ij}$  is the direct and  $I_{ij}$  is the indirect part of the photon propagator.<sup>19</sup>  $I_{ij}$  describes the electromagnetic field reflected from the surface. The direct part of the photon propagator in the case under consideration provides the so-called local-field correction of the molecular polarizability. It means that only the value  $I_{ij}(0, l, l, t-t')p_j^{(sp)}(t')$  remains in the integrand in Eq. (2.1). For convenience, the  $z$  arguments in the functions will be omitted, but they will be retained in the main expressions.

The energy of interaction between the dipole  $p_i^{(sp)}$  and the field induced by the polarization in the adsorbent, averaged over fluctuations of the dipole moment of the molecule, is

$$U_1 = -\frac{1}{2} \langle \mathbf{p}^{(sp)}(\mathbf{r}_a, t) \cdot \mathbf{E}^{(1)}(\mathbf{r}_a, t) \rangle. \quad (2.2)$$

Substitution of the expression for the field given by Eq. (2.1) into Eq. (2.2), and after a Fourier transformation over time, leads to the following expression:

$$U_1 = -\frac{1}{8\pi^2} \text{Re} \int d\omega G_{ij}^{\gg}(0, \omega) \langle p_i^{(sp)} p_j^{(sp)} \rangle_{\omega}, \quad (2.3)$$

where  $\langle p_i^{(sp)} p_j^{(sp)} \rangle_{\omega}$  is the spectral density of the correlation function<sup>12</sup>

$$\langle p_i^{(sp)}(t) p_j^{(sp)}(t') \rangle = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \langle p_i^{(sp)} p_j^{(sp)} \rangle_{\omega}. \quad (2.4)$$

Taking into account that the molecule is in equilibrium, the Callen-Welton theorem applies, e.g.,

$$\langle p_i^{(sp)} p_j^{(sp)} \rangle_{\omega} = i\hbar f(\omega) [(\alpha_{ji}^{(0)}(\omega))^* - \alpha_{ij}^{(0)}(\omega)], \quad (2.5)$$

with  $f(\omega) = 1/[1 - \exp(-2\beta)]$ ,  $\beta = \hbar\omega/2k_B T$ , and  $\alpha_{ij}^{(0)}(\omega)$  is the electric susceptibility (polarizability) of the isolated molecule. Using Eq. (2.5) we obtain

$$U_1 = -\frac{\hbar}{8\pi^2} \text{Re} \left\{ i \int d\omega f(\omega) G_{ij}^{\gg}(0, \omega) \times [(\alpha_{ji}^{(0)}(\omega))^* - \alpha_{ij}^{(0)}(\omega)] \right\}. \quad (2.6)$$

Thus, to calculate the first part of the interaction energy of the fluctuating dipole moment of the molecule with the nonequilibrium surface, one needs to know the electrodynamic Green's function of the nonequilibrium substrate,  $G_{ij}^{\gg}(\mathbf{r} - \mathbf{r}', l, l, \omega)$ . The notation “ $\gg$ ” in the Green's function means that both the source of the field and the observation point are situated in the upper half-space  $z > 0$ .

The presence of the spontaneous fluctuations in the adsorbent gives rise to the field at the point of location of the molecule,  $\mathbf{E}^{(sp)}(\mathbf{r}_a = 0, t)$ . This field induces an additional dipole moment at the site of the molecule,

$$p_i^{(ind)}(t) = \int dt' \alpha_{ij}^{(0)}(t-t') E_j^{(sp)}(t'). \quad (2.7)$$

The interaction energy between the induced dipole moment and the field generated by the spontaneous fluctuations of the polarization in the adsorbent can be written as

$$U_2(l) = -\frac{1}{2} \text{Re} \left\{ \int dt' \alpha_{ij}^{(0)}(t-t') \langle E_j^{(sp)}(t') E_i^{(sp)}(t) \rangle \right\}. \quad (2.8)$$

Since the fluctuating field is generated by the fluctuations of the currents in the substrate, the correlator of the “field-field” type can be written in terms of the Green's function and the correlator of the “current-current” type as

$$\begin{aligned} \langle E_j^{(sp)}(\mathbf{r}_a, t') E_i^{(sp)}(\mathbf{r}_a, t) \rangle &= \int d\mathbf{r}' d\mathbf{r}'' \int dz' dz'' \int dt'' dt''' \hat{A}(\mathbf{k}', \omega', \mathbf{r}_a - \mathbf{r}', t' - t'') G_{jk}^{(\prime)}(\mathbf{k}', z_a, z', \omega') \hat{A} \\ &\times (\mathbf{k}'', \omega'', \mathbf{r}_a - \mathbf{r}'', t - t''') G_{il}^{(\prime)}(\mathbf{k}'', z_a, z'', \omega'') \hat{A}(\mathbf{k}, \omega, \mathbf{r} - \mathbf{r}', t - t''') \left( \frac{1}{\omega^2} \right) \langle j_k(z') j_l(z'') \rangle_{\mathbf{k}, \omega}, \end{aligned} \quad (2.9)$$

where the notation “ $\langle \rangle$ ” means that the source of the field (fluctuating current) is situated in the sample ( $z < 0$ ) and the observation point is situated at  $z_a > 0$ .  $\hat{A}(\mathbf{k}, \omega, \mathbf{r} - \mathbf{r}', t - t')$  is an integral operator. Its action on an arbitrary function  $\phi(\mathbf{k}, \omega)$  is given by

$$\begin{aligned} \hat{A}(\mathbf{k}, \omega, \mathbf{r} - \mathbf{r}', t - t') \phi(\mathbf{k}, \omega) \\ = \int \frac{d\mathbf{k}}{4\pi^2} \int \frac{d\omega}{2\pi} e^{-i\mathbf{k}(\mathbf{r} - \mathbf{r}') + i\omega(t - t')} \phi(\mathbf{k}, \omega). \end{aligned} \quad (2.10)$$

Equation (2.9) shows that the problem of calculating the energy of interaction between fluctuating currents in the substrate and the molecular dipole moment is reduced to the calculation of the spectral density of the correlation function of the ‘‘current-current’’-type. The Fourier transformation of the correlation function is determined by

$$\langle j_k(\mathbf{r}, z, t) j_l(\mathbf{r}', z', t') \rangle = \hat{A}(\mathbf{k}, \omega, \mathbf{r} - \mathbf{r}', t - t') \times \langle j_k(z) j_l(z') \rangle_{\mathbf{k}, \omega}. \quad (2.11)$$

Thus, the adsorption potential may be written as

$$U(l) = U_1(l) + U_2(l), \quad (2.12)$$

with  $U_1(l)$  and  $U_2(l)$  given by Eqs. (2.6) and (2.8), respectively.

It should be noted that the structure of Eq. (2.12) derives from the fact that the van der Waals interaction between a particle and a substrate is caused by two fluctuating processes. These are both fluctuations of the molecular dipole moment and fluctuations of the electrical field in the nonequilibrium substrate. Since a fluctuating electric field in the substrate leads to an induced dipole moment at the molecule ( $p^{(\text{ind})} \sim E^{(\text{sp})}$ ), this leads to an interaction between the molecule and the substrate with the energy  $U_2$ . Fluctuations of the molecular dipole moment induce a polarization in the substrate. Their interaction is characterized by the energy  $U_1$ . It should be emphasized that the induced polarization (dipole moments) occurs in the nonequilibrium substrate. This explains the use of the Green’s function of the nonequilibrium substrate in Eq. (2.6). Both terms in Eq. (2.12), therefore, have characteristic features of a nonequilibrium substrate.

In the case of adsorption of a molecule on the surface of an equilibrium substrate, both expressions in Eq. (2.9) should be determined with the Green’s function of the equilibrium substrate. The second term transforms to

$$U_2(l) = -\frac{\hbar}{8\pi^2} \text{Re} \left\{ i \int d\omega f(\omega) \alpha_{ij}^{(0)}(\omega) \times [G_{ji}^*(0, \omega, l, l) - G_{ij}(0, \omega, l, l)] \right\}, \quad (2.13)$$

with

$$G_{ij}(0, \omega, l, l) = \int \frac{d\mathbf{k}}{4\pi^2} G_{ij}(\mathbf{k}, \omega, l, l). \quad (2.14)$$

Thus, the connections between interaction energy and photon propagator of a nonequilibrium substrate and correlators of ‘‘field-field’’ type [or ‘‘current-current’’ type, see Eq. (2.9)] were established in this part of the work. In this connection, it is necessary to mention three fundamental works of Agarwal<sup>21–23</sup> in which the properties of correlation functions of ‘‘field-field’’ type were studied. The fluctuation-dissipation theorem and Green’s-function method were used in these works. But only thermally equilibrium systems were discussed in Refs. 21–23. The wide spectrum of problems concerning van der Waals interaction between two bodies was considered by Agarwal. As opposed to Ref. 22, where a quantum approach was applied to both a particle and a field,

in the present work the electrodynamic Green’s function obtained in a classical approach will be used.

### III. ADSORPTION OF A MOLECULE ON A PLANE SURFACE OF A NONEQUILIBRIUM SEMICONDUCTOR

As discussed in the preceding section, the calculation of the van der Waals part of the adsorption potential is reduced to the calculation of the correlation function  $\langle j_k j_l \rangle$  for the nonequilibrium substrate with a plane interface. The calculation of the function  $\langle j_k j_l \rangle$  can be based on the results obtained in Ref. 24, where a procedure was developed to express the ‘‘current-current’’ correlator for a half-space in terms of the same correlator for the infinite medium. This procedure yields

$$\langle j_k(z) j_l(z') \rangle_{\mathbf{k}, \omega} = \int \frac{dq}{2\pi} [e^{-iq(z-z')} + p \zeta_l e^{-iq(z+z')}] \times \langle j_k j_l \rangle_{\mathbf{P}, \omega}. \quad (3.1)$$

In Eq. (3.1), the parameter  $p$  characterizes the processes of reflection of the particle from the plasma in the solid at the interface. For example, for specular reflection,  $p$  is equal to 1. The wave vector  $\mathbf{P} = (\mathbf{k}, q)$  is the three-dimensional wave vector, with  $\mathbf{k}$  the two-dimensional one lying in the plane of the adsorbent surface and  $q$  the vector component along the  $OZ$  direction. The parameter  $\zeta_l$  is equal to 1 in the case when  $l \neq z$  and is equal to  $-1$  when  $l = z$ . The value  $\langle j_k j_l \rangle_{\mathbf{P}, \omega}$  denotes the correlation function of the infinite nonequilibrium plasma.

In the absence of both an external magnetic field and a transport electrical current in the substrate, and in the case when the electron gas in the nonequilibrium substrate is homogeneous and nondegenerate, the ‘‘current-current’’ correlator for the infinite medium can be written as<sup>15</sup>

$$\langle j_k j_l \rangle_{\mathbf{P}, \omega} = \frac{2}{V} n e^2 D \delta_{kl}, \quad (3.2)$$

where  $n$  is the concentration of the electrons in the substrate,  $e$  is the electron charge,  $V$  is the volume of the substrate, and  $D$  is the diffusion coefficient. Equation (3.2) is the mathematical formulation of the ‘‘fluctuation-diffusion’’ theorem, analogous to the ‘‘fluctuation-dissipation’’ theorem (Callen-Welton theorem) for equilibrium systems. It should be mentioned that according to Ref. 15, expression (3.2) holds in the case when  $\omega \tau_1 \ll 1 \ll \omega \tau_0$ , where  $\tau_1$  is the time of dissipation of a pulse and  $\tau_0$  is the time of energy dissipation in the substrate. For a small nonelasticity of collisions between electrons and for rather high frequencies, the following inequality is fulfilled:  $\tau_0 \gg \tau_1$ . This means that Eq. (3.2) is valid for most cases of nonequilibrium substrates.

Taking into account Eqs. (3.1) and (3.2), Eq. (2.9) becomes

$$\begin{aligned} \langle E_j^{(\text{sp})}(\mathbf{r}_a, t') E_i^{(\text{sp})}(\mathbf{r}_a, t) \rangle &= \frac{2ne^2 D}{(2\pi)^4 V} \int dz' \int \frac{d\mathbf{k}}{4\pi^2} \frac{d\omega}{2\pi} e^{i\omega(t'-t)} G_{jl}^{(\prime)}(\mathbf{k}, z_a, z', \omega) \\ &\quad \times [G_{il}^{(\prime)}(-\mathbf{k}, z_a, z', -\omega) \pm p G_{il}^{(\prime)}(-\mathbf{k}, z_a, -z', -\omega)]. \end{aligned} \quad (3.3)$$

The upper sign in the brackets of Eq. (3.3) means that  $l \neq z$ , and the lower sign means  $l = z$ .

Thus, to solve the problem under consideration, one needs to know the Fourier components of the electrodynamic Green's function of a nonequilibrium substrate. In the framework of the dielectric formalism,<sup>25</sup> where the Green's function for a semi-infinite medium with a plane interface was calculated (see, for example, Refs. 26–28), the problem reduces to the calculation of the dielectric function for a non-

equilibrium semiconductor. Moreover, there are many calculations of dielectric functions for nonequilibrium semiconductors.<sup>29,30</sup>

It is quite natural to suppose that in the framework of the dielectric formalism, the electrodynamic Green's function of the nonequilibrium substrate has the same appearance as the Green's function of a substrate in equilibrium, with  $\vec{\epsilon}_{\text{eq}} \rightarrow \vec{\epsilon}_{\text{noneq}}$ . Therefore, we use the Green's function<sup>27</sup>

$$G_{ij}(\mathbf{k}, \omega) = \frac{1}{k^2} \begin{pmatrix} k_x^2 \tilde{\mathcal{J}}_{xx} + k_y^2 \tilde{\mathcal{J}}_{yy} & -k_x k_y (\tilde{\mathcal{J}}_{xx} - \tilde{\mathcal{J}}_{yy}) & -k_x k \tilde{\mathcal{J}}_{xz} \\ -k_x k_y (\tilde{\mathcal{J}}_{xx} - \tilde{\mathcal{J}}_{yy}) & k_y^2 \tilde{\mathcal{J}}_{xx} + k_x^2 \tilde{\mathcal{J}}_{yy} & -k_y k \tilde{\mathcal{J}}_{xz} \\ k_x k \tilde{\mathcal{J}}_{xz} & k_y k \tilde{\mathcal{J}}_{xz} & k^2 \tilde{\mathcal{J}}_{zz} \end{pmatrix}, \quad (3.4)$$

with  $\tilde{\mathcal{J}}_{mn}(\mathbf{k}, \omega)$  the components of the Green's function calculated in the  $s$ - and  $p$ -polarized waves representation. The plane of incidence is taken as the  $XOZ$  plane. Wave vector  $\mathbf{k}$  lies in the plane of the surface of the substrate.

To calculate the correlation function  $\langle E_i E_j \rangle$ , we need to calculate the integrals

$$\int d\mathbf{k} \int d\mathbf{k}' Q_{ji}(\mathbf{k}, \mathbf{k}'), \quad (3.5)$$

where

$$Q_{ji}(\mathbf{k}, \mathbf{k}') = \int_{-\infty}^{\infty} dq \int dz' dz'' G_{jk}^{(\prime)}(\mathbf{k}', z_a, z', \omega') G_{il}^{(\prime)}(\mathbf{k}'', z_a, z'', \omega'') [e^{-iq(z'-z'')} \pm p e^{-iq(z'+z'')}] \langle j_k j_l \rangle_{\mathbf{P}, \omega}. \quad (3.6)$$

It is clear from Eqs. (3.4)–(3.6) that when  $\langle j_k j_l \rangle_{\mathbf{P}, \omega} \sim \delta_{kl}$  [see Eq. (3.2)] the tensor  $Q_{ji}$  has only diagonal nonzero components. This follows from the integration over wave vectors  $\mathbf{k}'$  and  $\mathbf{k}''$  in Eq. (3.5) over the symmetrical region  $(-\infty, +\infty)$ .

It is convenient to rewrite Eq. (3.3) in the form ( $z_a = l$ ,  $l$  is the distance between the molecule and the surface)

$$\langle E_i^{(\text{sp})}(t') E_i^{(\text{sp})}(t) \rangle = \frac{2ne^2 D}{(2\pi)^5} \int d\omega e^{i\omega(t'-t)} [q_{ii}(l, \omega) \pm p f_{ii}(l, \omega)], \quad \begin{cases} i \neq z \\ i = z, \end{cases} \quad (3.7)$$

with

$$\begin{aligned} q_{ii}(l, \omega) &= \frac{1}{V} \sum_l \int dz' \int \frac{d\mathbf{k}}{4\pi^2} G_{il}^{(\prime)}(-\mathbf{k}, l, z', -\omega) G_{il}^{(\prime)} \\ &\quad \times (\mathbf{k}, l, z', \omega), \end{aligned} \quad (3.8)$$

$$\begin{aligned} f_{ii}(l, \omega) &= \frac{1}{V} \sum_l \int dz' \int \frac{d\mathbf{k}}{4\pi^2} G_{il}^{(\prime)}(-\mathbf{k}, l, -z', -\omega) G_{il}^{(\prime)} \\ &\quad \times (-\mathbf{k}, l, z', \omega). \end{aligned} \quad (3.9)$$

Taking into account that the main purpose of this study is to obtain a qualitative picture of the dependence of the adsorption potential on the distance between a molecule and a surface, we use a simple model for the adsorbent where the

Green's function has the form which was obtained in Ref. 27. The Green's function is dependent on the  $z$  coordinate via<sup>27</sup>

$$\tilde{\mathcal{J}}_{ii}(z) = P_{ii} e^{-i\eta_p z + i\eta_l} \quad (i = x, z), \quad S_{ii} e^{-i\eta_s z + i\eta_l} \quad (i = y), \quad (3.10)$$

where  $\eta_p$  and  $\eta_s$  are the  $z$  coordinates of the wave vector of  $p$ - and  $s$ -polarized waves in the substrate, respectively, and  $\eta$  is the  $z$  coordinate of the wave vector of the wave in vacuum.<sup>28</sup> The integration over  $z'$  in Eqs. (3.8) and (3.9) can be performed directly. As a result, four types of terms arise, namely the terms proportional to  $\delta$  functions  $\delta(\eta_p + \eta_s)$ ,  $\delta(\eta_p)$ , and  $\delta(\eta_s)$ , and the terms containing integrals of the form

$$a = \frac{1}{V} \int_{-\infty}^0 dz. \quad (3.11)$$

These integrals are formally infinite. Indeed, the term “semi-infinite medium” means that the dimension of the system along the  $OZ$  axis is so great that the bottom interface of the substrate does not influence the effects of adsorption on the upper interface. It means that Eq. (3.11) can be rewritten as

$$a = \frac{1}{V} \int_{-L}^0 dz = \frac{1}{S}, \quad (3.12)$$

where  $S$  is the area of the surface of the adsorbent. Since distances between a molecule and a surface are small, retardation processes can be neglected. Due to this, the integration over the pulse  $\mathbf{k}$  in Eqs. (3.8) and (3.9) can be easily performed. We obtain from Eqs. (3.8) and (3.9) that  $q_{ii}=0$ , and

$$f_{xx}(\omega) = \frac{9\pi}{8S} F_1 \frac{1}{l^4} - \frac{4\pi^4}{V} \left[ \left( \frac{\epsilon_{xx}}{\epsilon_{zz}} \right)^{1/2} - 1 \right]^{-1} F_2 \frac{1}{l} - \frac{3\pi\omega^4}{4c^4S} \text{Ei} \left( -\frac{2l}{L} \right), \quad (3.13)$$

$$f_{yy}(\omega) = f_{xx}(\omega), \quad (3.14)$$

$$f_{zz}(\omega) = \frac{3\pi}{S} F_3 \frac{1}{l^4}, \quad (3.15)$$

with

$$F_1 = \frac{1}{\epsilon_{zz}\epsilon_{xx} + 2\sqrt{\epsilon_{zz}\epsilon_{xx}} + 1}, \quad (3.16)$$

$$F_2 = \frac{\omega^2}{c^2} \frac{1}{\sqrt{\frac{\epsilon_{xx}}{\epsilon_{zz}} - 1}} \frac{1}{1 + \sqrt{\epsilon_{xx}\epsilon_{zz}}}, \quad (3.17)$$

$$F_3 = \left( \epsilon_{xx} + \frac{\epsilon_{xx}}{\epsilon_{zz}} \right)^{-2}. \quad (3.18)$$

It needs to be mentioned that Eqs. (3.10)–(3.15) apply to the case where the nonequilibrium semiconductor is anisotropic. In the case when the nonequilibrium state of the semiconductor is isotropic, the term  $\sim 1/l$  in Eqs. (3.13) and (3.14) disappears, but a term  $\sim 1/l^2$  appears. In Eq. (3.13),  $\text{Ei}(-x)$  indicates the exponential integral<sup>31</sup>

$$\int_x^\infty dt \frac{e^{-\mu t}}{t} = -\text{Ei}(-\mu x). \quad (3.19)$$

Substitution of Eqs. (3.13)–(3.15) into Eq. (3.7) gives

$$\langle E_i^{(\text{sp})}(t') E_j^{(\text{sp})}(t) \rangle = \frac{2ne^2pD}{(2\pi)^5} \int d\omega e^{i\omega(t'-t)} K_{ij}(\omega), \quad (3.20)$$

where

$$K_{ij}(\omega) = \begin{pmatrix} f_{xx}(\omega) & 0 & 0 \\ 0 & f_{yy}(\omega) & 0 \\ 0 & 0 & f_{zz}(\omega) \end{pmatrix}. \quad (3.21)$$

To obtain a qualitative dependence of the adsorption potential on the distance between the molecule and the surface of a nonequilibrium adsorbent, we use a simple model for the polarizability of the molecule. We shall assume that the molecule is isotropic, i.e.,  $\alpha_{ij}(\omega) = \alpha(\omega)\delta_{ij}$ .

According to Ref. 13, the first part of the adsorption potential, in the approximation where retardation effects are neglected, follows from Eq. (2.6). The result is

$$U_1(l) = -C \frac{1}{l^3}, \quad (3.22)$$

with

$$C = \frac{\hbar}{4} \int_0^\infty d\omega \text{cth}\beta \text{Im}(\alpha(\omega)) F_4(\omega), \quad (3.23)$$

$$F_4(\omega) = \frac{\sqrt{\epsilon_{xx}\epsilon_{zz}} - 1}{\sqrt{\epsilon_{xx}\epsilon_{zz}} + 1}. \quad (3.24)$$

As is clear from Eq. (3.22), the first part of the adsorption potential formally has the same form as the adsorption potential for a semiconductor in the equilibrium state.

Using Eqs. (3.12)–(3.15), (3.20), and (2.8), one obtains for the second part of the adsorption potential

$$U_2(l) = -D \left\{ C_1 \frac{1}{l^4} - C_2 \frac{1}{l} - C_3 \text{Ei} \left( -\frac{2l}{L} \right) \right\}, \quad (3.25)$$

where

$$C_1 = \frac{3ne^2p}{64\pi^4S} \int d\omega \alpha(\omega) [3F_1(\omega) - 4F_3(\omega)], \quad (3.26)$$

$$C_2 = \frac{4ne^2p}{(2\pi)^5} \int d\omega \alpha(\omega) F_2(\omega) F_3(\omega), \quad (3.27)$$

$$C_3 = \frac{3ne^2p}{(2\pi)^5S} \int d\omega \alpha(\omega). \quad (3.28)$$

It should be emphasized that in the case when adsorption occurs on the surface of an isotropic nonequilibrium semiconductor, the term  $\sim 1/l$  in the potential  $U_2$  is absent. But the term  $\sim 1/l^2$  arises. In this case,  $F_1 = F_3 = (\epsilon + 1)^2$ , and  $C_1 < 0$ . This means that the term  $\sim 1/l^4$  in the adsorption potential becomes repulsive.

Equations (3.22) and (3.25) give the expression for the adsorption potential on the surface of a nonequilibrium semiconductor,

$$U(l) = -C \frac{1}{l^3} - D \left\{ C_1 \frac{1}{l^4} - C_2 \frac{1}{l} - C_3 \text{Ei}(-2l/L) \right\}. \quad (3.29)$$

Equation (3.29) is the main result of this work.

#### IV. DISCUSSION

The van der Waals component of the adsorption potential for the surface of a nonequilibrium semiconductor was obtained in Sec. III. It is very different from the corresponding result for an equilibrium semiconductor. Essential features of

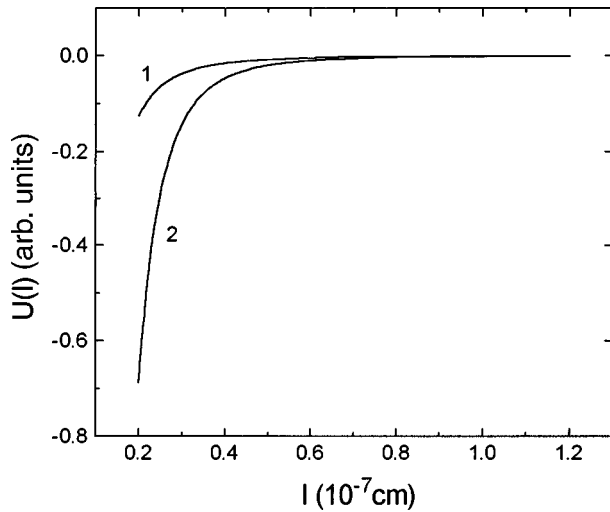


FIG. 1. Sketch of the attractive part of the adsorption potential. Curve 1 corresponds to an equilibrium and curve 2 corresponds to a nonequilibrium substrate.

the adsorption of a molecule on the surface of a nonequilibrium semiconductor are, first, the existence of the terms  $\sim 1/l^4$  and  $1/l$  (or  $1/l^2$  in the case of an isotropic nonequilibrium state) and, second, the appearance of the sign “+” in the terms proportional to  $1/l$  and  $\text{Ei}(-2l/L)$ . The latter means that the van der Waals interactions do not only have an attractive part. A repulsive part of the potential is also formed by the van der Waals interaction. It should be mentioned that the attractive part of the adsorption potential is formed by the van der Waals interactions in equilibrium.<sup>12,13</sup> For adsorption on a nonequilibrium semiconductor, the behavior of the total adsorption potential can be very different. Namely, coefficient  $C_1$  in Eq. (3.29) may be both positive or negative. In the latter case, a molecule cannot be adsorbed on the surface. For example, if coefficients  $C$  and  $C_1$  are the same order of magnitude, the term proportional to  $l^{-4}$  can be the same order of magnitude as the term proportional to  $l^{-3}$ . This means that the repulsive part of the adsorption potential will dominate the attractive part (due to the term proportional to  $l^{-1}$ ), and adsorption of the molecule will not occur.

In Fig. 1, the attractive part of the adsorption potentials on the surface of nonequilibrium and equilibrium semiconductors is shown. It needs to be emphasized that the last term of Eq. (3.29) slowly changes at distances of about  $10^{-7}$  cm. It allows us to neglect this term in the calculations. In Fig. 2, a sketch of the total adsorption potential including the short-range repulsive part of (see, for example, Ref. 32)

$$U_{\text{rep}}(l) = C_r \frac{1}{l^9} \quad (4.1)$$

is shown. For both Figs. 1 and 2, we used positive values for the coefficients  $C$ ,  $C_1$ ,  $C_2$ , and  $C_3$ .

As was mentioned above, there is a possibility of an isotropic nonequilibrium state in the substrate. For this case, the adsorption potential can be expressed in the form

$$U(l) = -C \frac{1}{l^3} - D \left\{ C_1 \frac{1}{l^4} - \tilde{C}_2 \frac{1}{l^2} - C_3 \text{Ei}(-2l/L) \right\}, \quad (4.2)$$

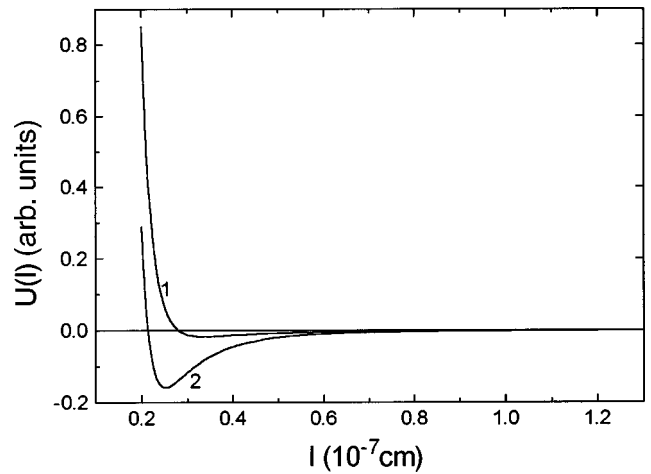


FIG. 2. Sketch of the total adsorption potential calculated for an equilibrium (curve 1) and a nonequilibrium (curve 2) substrate.

with

$$\tilde{C}_2 = \frac{ne^2 p}{32\pi^2 S} \int \frac{\omega^2 d\omega}{c^2} F_5(\omega), \quad (4.3)$$

$$F_5(\omega) = \frac{2\alpha(\omega)}{\varepsilon(\omega) + 1}. \quad (4.4)$$

It is clear from Eq. (4.2) that the behavior of coefficient  $\tilde{C}_2$  essentially depends on the pole part of  $F_5(\omega)$ , i.e., its value and sign are defined by properties of the dielectric function of the nonequilibrium adsorbent.

It is interesting to study the approach to the equilibrium state in Eq. (3.25). As mentioned above, in the equilibrium state Eq. (2.8) transforms into Eq. (2.13). It immediately leads to the transformation of Eq. (3.25) to a form similar Eq. (3.22). The value of  $F_4(\omega)$  which determines the coefficient  $C$  will contain the dielectric function of the semiconductor in equilibrium. It needs to be emphasized that the common form of the nonequilibrium terms ( $\sim D$ ) in Eqs. (3.25), (3.29), and (4.2) is determined by the universal character of the “fluctuation-diffusion” theorem. Values of the coefficients  $C_1$ ,  $C_2$ ,  $C_3$ , and  $C$ , however, depend on the kind of nonequilibrium state of the substrate. Clearly, all these coefficients are defined by the dielectric function of the nonequilibrium semiconductor. The volume  $V$  of an adsorbent and the area  $S$  of its surface in the denominators of the expressions for  $C_i$  appear due to the presence of  $V$  in Eq. (3.2). This fact has a clear physical interpretation: when the volume of a sample increases, the correlations of the fluctuation currents decrease.

As was mentioned above, the classical electrodynamic Green’s function was used in the calculation of “current-current” correlators in the present work. But, as was shown in previous works (for example, using the functional of the particle density method<sup>33</sup> or the classical semiempirical approach),<sup>34</sup> microscopical and classical approaches give qualitatively similar results. Therefore, it can be assumed that the results obtained in the present work give us qualitatively correct results.

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